

FINAL TECHNICAL REPORT

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SUMMARY OF RESEARCH /PUBLICATIONS FOR FINAL GRANT PERIOD

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INVENTION STATEMENT

THERE HAVE BEEN NO INVENTIONS CONNECTED WITH THIS RESEARCH

FINAL TECHNICAL REPORT

1 "Comment on broadening of water microwave lines by collisions with helium atoms." S. Maluendes, A. D. McLean, and S. Green, J. Chem. Phys. **96**, 8150 (1992).

Theoretical descriptions of interaction forces and collision dynamics in the H₂O-He system were improved by calculating the interaction at additional orientations and by including diffuse functions in the basis set. The improvements made substantial changes to the potential energy surface, but made only small changes in the predicted microwave pressure broadening coefficients.

2. "Calculations of ion-molecule deuterium fractionation reactions involving HD." S. A. Maluendes, A. D. McLean, and E. Herbst, Astrophys. J. **397**, 477 (1992).

Gas-phase chemical models of deuterium fractionation in dense interstellar clouds utilize a small number of exothermic reactions to achieve fractionation. Although HD is a major repository of deuterium, it does not appear to exchange D with many molecular ions. The potential energy surfaces of three representative protonated ions (H₃⁺, CH₃⁺, HCO⁺) and HD were investigated. Quantum chemical calculations confirmed an earlier semi-quantitative explanation for the fractionation processes and showed that tunnelling at low temperature is unlikely to alter this picture. Fractionation reactions proceed to products when the transition state lies below the energy of the reactants. Reactivity can be therefore be predicted by computing the activation energy with *ab initio* calculations.

3. "*Ab initio* predictions on the rotational spectra of carbon-chain carbene molecules." S. Maluendes and A. D. McLean, Chem. Phys. Lett. **200**, **511** (1992).

Rotational constants for the carbon-chain molecules H₂C=(C=)_nC, n=3-8, were predicted using *ab initio* methods. H₂C₃ and H₂C₄ have already been observed by radioastronomy. Our calculated dipole moments indicate that the higher members in the series are good candidates for future astronomical or laboratory searches.

4. "Theoretical IR spectra of ionized naphthalene." F. Pauzat, D. Talbi, M. D. Miller, D. J. DeFrees, and Y. Ellinger, J. Phys. Chem. **96**, 7882 (1992).

Ab initio molecular orbital theory was used to study the effect of ionization on the infrared spectrum of naphthalene. The structures, band frequencies, and intensities of neutral and ionized naphthalene were determined. The calculated frequencies and intensities allowed an assignment of the most important bands in the newly reported experimental spectrum of the cation. Agreement between theory and experiment is sufficient to confirm that ionization significantly affects intensities without dramatically shifting the positions of the ir bands. These results suggest that it is no longer necessary to postulate that PAHs are stripped of most of their hydrogens to explain the observed ratio of carbon skeleton band intensities to CH stretching ones.

5. "Improved collisional excitation rates for interstellar water." S. Green, S. Maluendes, and A. D. McLean, *Astrophys. J. Suppl. Ser.* **85**, 181 (1993).

Theoretical rate constants among the lowest 45 para and 45 ortho rotational levels of water in collisions with He atoms have been calculated for temperatures between 20 and 2000 K using a new theoretical potential (described above). These values are 30-40% larger than previous ones but relative sizes of state-to-state rates have not changed significantly.

6. "Calculations on the competition between association and reaction for $C_3H^+ + H_2$." S. A. Maluendes, A. D. McLean, K. Yamashita, and E. Herbst, *J. Chem. Phys.* **99**, 2812 (1993).

A potential energy surface has been determined for the competing associative and reactive ion-molecule processes involving C_3H^+ and H_2 . Our *ab initio* results show that the linear C_3H^+ ion and H_2 can directly access the deep potential well of the propargyl ion H_2CCCH^+ , which lies 390 kJ mol^{-1} below the reactants. The more stable cyclic $c\text{-}C_3H_3^+$ ion lies 501 kJ mol^{-1} below the reactants. Isomerization between the linear and cyclic structures can occur via two pathways, one involving a single transition state and the other possessing two transition states and an intermediate. The dissociation of $c\text{-}C_3H_3^+$ to $C_3H_2^+ + H$ proceeds without a barrier, but is endothermic with respect to the reactants by 7.3 kJ mol^{-1} . Rates and branching ratios calculated with the *ab initio* data are in agreement with some experimental observations and in disagreement with others.

7. Theoretical infrared spectra of some model polycyclic aromatic hydrocarbons: effect of ionization." D. J. DeFrees, M. D. Miller, D. Talbi, F. Pauzat, and Y. Ellinger, *Astrophys. J.* **408**, 530 (1993).

In order to test the hypothesis that polycyclic aromatic hydrocarbons (PAHs) are carriers of the UIR bands, we studied selected small PAHs in order to ascertain the effect of ionization upon their IR spectra. In this work we determined the IR spectra of naphthalene, anthracene, and pyrene and their cations by means of *ab initio* calculations. The frequencies of the cations are shifted only slightly with respect to the neutrals, while the band intensities are strongly affected. The calculated CH/CC vibrational intensity ratios of the ions are in much better agreement with those deduced from observation than are those of the neutrals.

8. "Calculations concerning interstellar isomeric abundance ratios for C_3H and C_3H_2 ." S. A. Maluendes, A. D. McLean, and E. Herbst, *Astrophys. J.* **417**, 181 (1993).

The syntheses of interstellar $c\text{-}C_3H_2$, H_2CCC , $c\text{-}C_3H$, and $HCCC$ (where "c" indicates a cyclic isomer) are thought to proceed via dissociative recombination of the precursor ions $c\text{-}C_3H_3^+$ and H_2CCCH^+ , which are in turn produced mainly via the radiative association reaction between C_3H^+ and H_2 . We have utilized *ab initio* methods to study the potential energy surface for $C_3H^+ + H_2$ to form the isomers $c\text{-}C_3H_3^+$ and H_2CCCH^+ . The overall rate coefficient for radiative association has been calculated as a function of temperature via the phase space method. Our *ab initio* calculations show that the H_2CCCH^+ isomer is formed directly without an activation barrier and that isomerization can occur readily via a low-energy pathway. Calculation of the equilibrium coefficient for $H_2CCCH^+ \rightleftharpoons c\text{-}C_3H_3^+$ as a function of temperature shows that equal abundances of these two ions should

be produced as relaxation proceeds, in agreement with experimental measurements at high pressure.

9. "New calculations on the ion-molecule processes $\text{C}_2\text{H}_2^+ + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H}$ and $\text{C}_2\text{H}_2^+ + \text{H}_2 \rightarrow \text{C}_2\text{H}_4^+$." S. A. Maluendes, A. D. McLean, and E. Herbst, Chem. Phys. Lett. **217**, 571 (1994).

New quantum chemical calculations have been undertaken to understand the rates and mechanisms of the reactive and associative channels for $\text{C}_2\text{H}_2^+ + \text{H}_2$. The reactive channel, which produces $\text{C}_2\text{H}_3^+ + \text{H}$, was found to be slightly endothermic, confirming earlier calculations and in agreement with recent experimental work. The associative channel leading to C_2H_4^+ proceeds via a transition state that lies below the energy of the reactants, so association is expected to be efficient. This result is in conflict with an earlier theoretical study but in agreement with low temperature experimental measurements.

10. "Anisotropic rigid rotor potential energy function for $\text{H}_2\text{O}-\text{H}_2$." T. R. Phillips, S. Maluendes, A. D. McLean, and S. Green, J. Chem. Phys. **101**, 5824 (1994).

We have calculated the interaction for $\text{H}_2\text{O}-\text{H}_2$ at 722 points on a five-dimensional surface where both molecules are treated as rigid rotators. The *ab initio* points were fit with a 48-term angular expansion of spherical harmonics and rotation matrices. The potential functions shows strong angular dependence and a large contribution from electrostatic contributions. When averaged over H_2 orientations, the resulting surface is found to have a zero-crossing point and a minimum at distances similar to the corresponding $\text{H}_2\text{O}-\text{He}$ surface but is more repulsive at short range and more attractive at long range. The isotropic potential has zero-crossing radius of $r = 3.05 \text{ \AA}$ and a well depth of $D = 49.5 \text{ cm}^{-1}$ at $R_m = 3.52 \text{ \AA}$.

11. "A correlated *ab initio* study of linear carbon-chain radicals C_nH ($n=2-7$)." D. E. Woon, Chem. Phys. Lett. **244**, 45 (1995).

Linear carbon-chain radicals C_nH for $n=2-7$ were studied with correlation consistent valence and core-valence basis sets and the coupled cluster method RCCSD(T). Equilibrium structures, rotational constants, and dipole moments were determined and compared with available experimental data. The ground state of the even- n series changes from 2^+ to 2^- as the chain is extended. For C_4H , the 2^+ state was found to lie just 72 cm^{-1} below the 2^- state in the estimated complete basis set limit for valence correlation. Core-valence effects stabilize the 2^+ state by at least another 140 cm^{-1} , however, making the assignment more definitive. The C_2H^- and C_3H^- anions have also been characterized.

12. "*Ab initio* characterization of MgCCH , MgCCH^+ , and MgC_2 and pathways to their formation in the interstellar medium." D. E. Woon, Astrophys. J. **456**, 602 (1996).

An extensive study of Mg-bearing compounds was performed in order to determine molecular properties critical for planning and executing new astronomical searches and laboratory studies. The primary focus of the work was on MgCCH , MgCCH^+ , and the isomers of MgC_2 . Only MgCCH has been identified in laboratory studies. Additional calculations were carried out on MgH , MgNC , MgCN , and their cations in an effort to

evaluate pathways to the formation of MgCCH and MgCCH⁺ in the ISM or in circumstellar envelopes. Correlated *ab initio* methods and correlation consistent basis sets were employed. Properties including structures, rotational constants, dipole moments, and harmonic frequencies were determined. The transition state between linear MgCC and cyclic MgC₂ was characterized and found to yield a minimal barrier (~0.5 kcal/mol), indicating easy interconversion of the linear isomer to the more stable cyclic form. Direct reactions in the ISM between ground state Mg or Mg⁺ and HCCH are precluded by their large endothermicity, but a number of ion-molecule or neutral-neutral reactions exchange reactions between CCH and various Mg-containing species offer plausible pathways to MgCCH and MgCCH⁺. Weakly bound MgH may react with CCH to form MgCCH, but MgH has not been detected. Both MgNC and MgCN have been observed, but their reactions with CCH are slightly endothermic by 1-3 kcal/mol. Although MgH⁺, MgNC⁺, and MgCN⁺ have not been detected, their reactions with CCH to form MgCCH⁺ are all exothermic. With only a small barrier separating linear MgCC and cyclic MgC₂, the dissociative recombination of MgCCH⁺ with an electron is expected to yield cyclic MgC₂ and regenerate Mg and CCH. New astronomical searches for MgCCH, MgCCH⁺, cyclic MgC₂, MgNC⁺, and MgCN⁺ will provide further insight into organo-magnesium astrochemistry.

13. "Why HOC⁺ is detectable in interstellar clouds: The rate of the reaction between HOC⁺ and H₂." E. Herbst and D. E. Woon, *Astrophys. J.* **463**, L113 (1996).

The recent confirmation of by Ziurys and Apponi of the detection of HOC⁺ toward Sgr B2 (OH) and their identification of the ion in Orion-KL and several other sources show that HOC⁺ is far more abundant than predicted by previous ion-molecule models. In these models, the reaction HOC⁺ + H₂ → HCO⁺ + H₂ is assumed to rapidly destroy HOC⁺, based on the results of a prior calculation. We have recalculated the rate of this reaction as a function of temperature using a new *ab initio* potential surface and a phase space approach to the dynamics which includes tunneling. The new calculated rate is small (<1 × 10⁻¹⁰ cm³ s⁻¹) at temperatures under 100 K.

14. "A correlated *ab initio* study of the *X*²A₁ and *A*²E states of MgCH₃." D. E. Woon, *J. Chem. Phys.*, **104**: 9495 (1996).

The *X*²A₁ and *A*²E states of the MgCH₃ radical have been studied with correlation consistent basis sets and the coupled cluster method RCCSD(T) in order to compare with two recent experimental efforts. The best computed values [RCCSD(T)/cc-pCVTZ] for the *X*²A₁ state are (experimental results in parentheses): A_e = 160.433 GHz, B_e = 10.948 GHz (B₀ = 11.008 GHz), and *c*_e = 1.011 D. Values for the *A*²E state are A_e = 154.648 GHz (A₀ = 149.666 GHz), B_e = 10.87 GHz (B₀ = 10.932 GHz), and *c*_e = 1.022 D. The excitation energy (T_e) for the *A*²E to *X*²A₁ transition is 19 999 cm⁻¹ (T₀₀ = 20 030 cm⁻¹). A brief discussion of bonding trends in Mg-containing radicals is included.

15. "On the stability of interstellar carbon clusters: The rate of the reaction between C₃ and O." D. E. Woon and E. Herbst, *Astrophys. J.*, **465**: 795 (1996).

New experimental results on the rates of selected neutral-neutral reactions involving either gas-phase atoms (C) or radicals (OH, CN) show that these reactions are much more

rapid than previously thought. It is currently unclear, however, how general these results are. The results of chemical models of dense interstellar clouds are strongly affected by the inclusion of rapid neutral-neutral gas-phase reactions, most of which have not yet been studied in the laboratory. Unstudied reactions involving atomic oxygen and carbon clusters are known to curtail the synthesis of complex molecules if they occur rapidly at low temperatures. In this work, we show via quantum chemical and dynamical studies that the prototype reaction between O and C₃ possesses a small activation barrier and does not occur rapidly at low temperatures even when tunneling is considered.

16. "Relative rates for the cyclization of C₂N and C₂P." D. E. Woon and E. Herbst, in preparation.

Although the most stable isomers of C₂N and C₂P are linear ² radicals, both have cyclic isomers that lie relatively close in energy. At the RCCSD(T)/cc-pVTZ level, the cyclic isomers lie above the linear forms by only 11.1 and 5.1 kcal/mol for C₂N and C₂P, respectively. However, the barriers for cyclization are very different, with that of C₂N (49.3 kcal/mol) much larger than that of C₂P (15.3 kcal/mol). Rate calculations were performed to estimate the yield of each isomer from a process that might generate hot C₂N or C₂P such as the dissociative recombination of HCCN⁺ or HCCP⁺ with an electron. In spite of the differences in the potential energy surfaces, the yields are about 30% cyclic, 70% linear for both species.

17. "The rate of the reaction between CN and C₂H₂ at interstellar temperatures." D. E. Woon and E. Herbst. in preparation.

The rate coefficient for the important interstellar reaction between CN and C₂H₂ has been calculated as a function of temperature between 10 K and 300 K. The potential energy surface has been determined via *ab initio* quantum chemical techniques. It exhibits no barrier in the entrance channel but does show a small exit channel barrier that lies below the energy of the reactants. Phase space calculations, which take the exit channel barrier into account, show the same unusual temperature dependence as determined by experiment, in which the rate coefficient first increases as the temperature is reduced below room temperature and then starts to decrease at temperatures below 100 K. Overall agreement between theory and experiment is excellent and confirms that the reaction is competitive with ion-molecule processes at cold interstellar temperatures.